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## (54) PRODUCTION OF CARRIED CATALYST

## (57)Abstract:

PURPOSE: To produce a catalyst using a metal oxide, which is capable of setting the particle diameter of a catalytic material regardless of the carried quantity of the catalytic material, has uniform quality, is free from the change of the particle diameter of the catalyst in producing the catalyst and has long service life and high activity.

CONSTITUTION: This producing method of the carried catalyst includes a process for forming a colloidal metal oxide particle by hydrolyzing a metallic alkoxide to be a raw material of the carrier in a dispersed solution of a super fine particle having catalytic activity while stirring in the presence of water. The dispersed solution of the super fine particle is formed by using a micro-emulsion, in which an aq. solution containing a water soluble metallic compound is present as a droplet in super fine particle state, as the raw material of the dispersed solution of the super fine particle and insolubilizing the water soluble metallic compound contained in the droplet. The water soluble metallic compound is insolubilized by reduction reaction.

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**CLAIMS**

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[Claim(s)]

[Claim 1] The manufacture approach of the support catalyst characterized by including the process which it hydrolyzes [ process ] under existence of water under churning of the metal alkoxide used as a support raw material, and makes the metallic-oxide particle of colloid generate in the dispersion liquid of the ultrafine particle which has catalytic activity.

[Claim 2] The manufacture approach of the support catalyst indicated to claim 1 which uses as a raw material the microemulsion in which the water solution with which the dispersion liquid of an ultrafine particle contain water-soluble metallic compounds exists as an ultrafine particle-like drop, and is characterized by insolubilizing the water-soluble metallic compounds contained in this drop, and being made.

[Claim 3] The manufacture approach of the support catalyst indicated to claim 2 characterized by being what insolubilization of water-soluble metallic compounds depends on a reduction reaction.

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

It is field-of-the-invention] to up [ [industrial ]. This invention relates to the manufacture approach of the support catalyst which distributed the ultrafine particle which has metaled catalytic activity.

[0002]

[Description of the Prior Art] As everyone knows, since a reaction advances on a catalyst front face, the researcher of this direction is searching for the large catalyst of surface activity the catalytic reaction which uses a heterogeneous catalyst by trial and error. In this case, since activity becomes high so that surface area is large, if the amount and the quality of an active substance per unit surface area are the same, inorganic oxide gel like a silica with large surface area or an alumina is used for the support of the catalyst matter in many cases. And although the general manufacture approach of said inorganic oxide gel is the approach of calcinating and dehydrating the inorganic oxide gel obtained by hydrolysis of mineral salt, also when inorganic ion, such as sodium which originates in a raw material salt or a hydrolysis reagent by this approach, carries out minute amount mixing unescapable and this affects the activity and the physical properties of a catalyst, there are not. [ few ] Moreover, although the inorganic oxide gel obtained by the aforementioned approach is made to support the catalyst matter with the sinking-in method in many cases, it is most difficult to acquire a catalyst with a homogeneous front face by this approach. Furthermore, in the conventional method, there is also a problem on which the particle size of a catalyst metal becomes settled in the amount of metal support, and the technique in which particle size can be set up regardless of the amount of metal support is searched for.

[0003] since the heterogeneity of said front face carried out makes theoretical retrieval of a heterogeneous catalyst difficult and this has barred catalyst development and development of the catalyst theory -- homogeneous -- high -- development of an activity catalyst was ancient times to a catalyst researcher's technical problem. And it also turns out that many of catalyst front faces currently considered to be homogeneity by development of analytical skill are heterogeneity, and development of this catalyst is not progressing. This cause is said for the crystal of the catalyst matter which deposits from a solution to change greatly on the pore configuration, the magnitude, and the crystal deposit conditions of a carrier surface in case the catalyst matter is supported with the sinking-in method to support. The alkoxide method has been attracting attention as the preparation approach of a homogeneous catalyst from before for about ten years. Manufacture of the metal support catalyst by this approach dissolves a metal salt in a hydrophilic organic solvent with coordination ability, such as a glycol, after it adds the fusibility alkoxide of metals, such as aluminum and silicon, to this solution and using it as homogeneity liquid, it changes this alkoxide into the metallic-oxide colloid which hydrolyzes and ripens and corresponds, and it is performed by carrying out hydrogen reduction of this product after desiccation / baking. By this approach, the gel formed by desiccation and baking of metallic-oxide colloid serves as support, and the metal obtained by this by the hydrogen reduction of a metal salt is supported, and it becomes a catalyst.

[0004] As for the metal support catalyst by the alkoxide method, many patents and reports are announced with progress of research. For example, the metal support alkoxide method zirconia catalyst of various kinds [ catalyst / of various kinds / alumina catalyst / of various kinds / catalyst / of various kinds / JP,63-45620,B / method / of the benzene by the alkoxide method silica catalyst which supported a ruthenium and copper to JP,60-59215,B / partial hydrogenating / metal support alkoxide method silica / metal support alkoxide method / metal support alkoxide method titania ] is indicated by JP,63-45623,B at JP,63-45621,B at JP,63-45622,B. Moreover, Ueno and others is J.Chem.Soc. Faraday Trans.I Minakami and others has released the research report of the alkoxide method catalyst to J.Chem.Tech.Biotechnol.36 236 (1986) etc. 79 127 (1983) etc.

[0005] Although many metal support alkoxide method catalysts are announced as mentioned above, since this alkoxide

is hydrolyzed and this catalyst is prepared after it dissolves a metal alkoxide in metal salting in liquid, the reduction process which converts a metal salt into a metal is required for it. Since the metal salt in the particle obtained by hydrolysis and desiccation of an alkoxide in the top which needs elevated-temperature processes, like this reduction process carries out hydrogen reduction of the metal salt currently distributed in a metallic oxide above 100 degrees C sticks to the metallic-oxide gel which generated by hydrolysis of an alkoxide or it exists in the condition dissolved in the structure underwater which this metallic-oxide gel holds etc., it is not avoided that the ultra-fine particle formed at a reduction process becomes heterogeneity. That is, even if it makes the dispersing element of a sufficiently homogeneous metal salt form by the alkoxide method, metal particle size will become heterogeneity in the process in which a metal salt is returned to a metal. Moreover, since a metal salt generally has chemical activity stronger than a metal, when the metal which association may be formed between the metallic oxides and metal salts used as support, therefore has catalytic activity by reduction of a metal salt is made to form, the property of this metal proper may be spoiled or heterogeneous activity may be added.

[0006] By the approach of using as a raw material the microemulsion which the ultrafine particle manufacturing method is also studied from before in the field of colloid chemistry etc., for example, is progressing quickly on the other hand recently, the example of production of the ultra-fine particle metallurgy group compound ultrafine particle of the diameter of several angstroms - 10A of numbers is announced [USP 4,425,261(1984); Colloids Surface 5 209 (1982) etc.]. This approach is an approach of making the drop of the magnitude of the request containing the metal salt of the amount of requests forming into an oil, returning this metal salt from a hydrazine, hydrogen, etc., and obtaining an ultra-fine particle from the metal salt water solution, surfactant, and oil of an ultrafine particle raw material. The ultra-fine particle is expected as a future functional material, the manufacture approach etc. is examined by our country as a national project, and the method of obtaining an ultra-fine particle from metallic fumes etc. is announced. moreover -- the manufacture approach of an ultrafine particle, and physical properties -- chemistry -- the total -- a full account is given by opinion No.48 (edited by Chemical Society of Japan, 1985 issue).

[0007]

[Problem(s) to be Solved by the Invention] This invention solves many aforementioned problems looked at by the manufacture approach of the catalyst by the conventional alkoxide method, and makes it the technical problem to offer the manufacture approach of a support catalyst excellent in the catalyst engine performance with which the ultrafine particle is supported.

[0008]

[Means for Solving the Problem] this invention persons came to complete this invention, as a result of repeating research wholeheartedly that said technical problem should be solved. That is, according to this invention, in the dispersion liquid of the ultrafine particle which has catalytic activity, it hydrolyzes under existence of water under churning of the metal alkoxide used as a support raw material, and the manufacture approach of the support catalyst characterized by including the process which makes a colloid metallic-oxide particle generate is offered. Moreover, according to this invention, the microemulsion in which the water solution with which the dispersion liquid of an ultrafine particle contain water-soluble metallic compounds exists as an ultrafine particle-like drop is used as a raw material, and the manufacture approach of the aforementioned support catalyst characterized by insolubilizing the water-soluble metallic compounds contained in this drop, and being made is offered. Furthermore, according to this invention, the manufacture approach of the aforementioned support catalyst characterized by being what insolubilization of water-soluble metallic compounds depends on a reduction reaction is offered.

[0009] In this invention, the ultrafine particle dispersion liquid used as the preparation raw material of a support catalyst are the liquid which carried out homogeneity distribution of the ultrafine particle with catalytic activity at the dispersion medium. The mixed liquor of the organic solvent which the liquid used as a dispersion medium does not react with the ultrafine particle to distribute, does not dissolve this particle, but may dissolve the metal alkoxide to be used or this solvent, and water is used. Moreover, in order to make these dispersion liquid distribute an ultrafine particle to stability, dispersion-liquid weight can make a surfactant contain 4 to 20% preferably 0.5 to 40%. Generally the ultrafine particle content in dispersion liquid is 0.1 - 1 % of the weight preferably 0.0001 to 3% of the weight. Moreover, dispersion liquid can mix the ultrafine particle, dispersion medium, and surface active agent of the specified quantity, and can obtain them by distributing an ultrafine particle in a dispersion medium using powerful dispersers, such as a jet mill and a ball mill.

[0010] As an ultrafine particle which has catalytic activity, as long as it has catalyst ability, what kind of thing may be used, and various ultrafine particles, such as metallic compounds, such as transition metals, a metal especially chosen from a V group - VIII group's transition metals, and a metallic-oxide metallurgy group sulfide, or an insoluble metal salt, can be used for such a thing. Moreover, the aforementioned ultrafine particle may be independent, or two or more

sorts may use, mixing, and the example of the partial hydrogenation catalyst of the benzene containing the mixture of ultrafine particle-like copper and an ultrafine particle-like ruthenium etc. is given as an example of two or more sort mixing use.

[0011] The ultrafine particle used by this invention can be manufactured by various approaches, such as the approach of making it form by gaseous phase reaction, such as an approach of oxidizing [ oxidize and its reduction-processes ] the microemulsion containing \*\* water solubility compound, a method of quenching \*\* steam, \*\* gaseous-phase pyrolysis, and vapor phase oxidation. The ultrafine particle obtained by the approach of \*\* and \*\* among said manufacture approaches can obtain dispersion liquid by making a dispersion medium distribute this. It is also possible to be able to use as ultrafine particle content dispersion liquid which use this by this invention as it is, to add an organic solvent and water if needed, and to use as ultrafine particle content dispersion liquid of this invention on the other hand, since an ultrafine particle is obtained with the gestalt of ultrafine particle dispersion liquid by the approach of \*\*.

[0012] instantiation of the organic solvent used as the dispersion medium of ultrafine particle dispersion liquid mentions aliphatic series ketones [ , such as comparatively long-chain aliphatic series monohydric-alcohol; acetones, such as hydrocarbon; hexanols, such as a cyclohexane, cycloheptane, n-hexane, n-heptane, an isooctane, n-Deccan, benzene, and a xylene, heptanol and an octanol, and a methyl ethyl ketone, ]; etc. These solvents may be independent, or they may be used, mixing. Especially the surfactant used for ultrafine particle dispersion liquid is not limited, but can use the surfactant of cation nature, anion nature, nonionic, and both sexes. As the example, the polyethylene-glycol-p-nonylphenyl ether, pentaethylene glycol dodecylether, the G 2-ethylhexyl sulfo sodium succinate, a cetyl trimethylammonium star's picture, etc. are illustrated.

[0013] The support catalyst manufactured by this invention is a catalyst which made the metallic-oxide colloidal particle obtained by hydrolysis of a metal alkoxide support the ultrafine particle which has the catalytic activity of a metal metallurgy group oxide etc. Moreover, this catalyst is a catalyst more highly efficient than the catalyst manufactured with a conventional method in the field of far-reaching catalytic reaction. For example, with the support catalyst containing the vanadium, Lynn, and oxygen which are used in case a partial oxidation product is manufactured by oxidization of an alkane, a catalyst with sharply high selectivity can be manufactured from the catalyst manufactured with a conventional method. Moreover, a catalyst with sharply high selectivity can be manufactured from the catalyst with which it is manufactured with a conventional method also in the rhodium catalyst used in case a with a carbon numbers of two or more compound is manufactured by partial hydrogenation of a carbon monoxide. Furthermore, since the catalyst of high activity can be sharply manufactured from the catalyst manufactured with a conventional method in the platinum catalyst for complete oxidation of a hydrocarbon, it is the manufacture approach of the suitable catalyst for manufacture of the combustion catalyst it is expected that future development is.

[0014] as mentioned above, the field of the various catalytic reaction in this invention -- it is -- a conventional method -- high selectivity -- or -- high -- since an activity top can be provided with a long lasting catalyst, a catalyst manufacture raw material is an approach desirable as the manufacture approaches, such as an expensive noble-metals support catalyst. Moreover, most catalysts manufactured by this invention are catalysts containing a metallic element, and it is the manufacture approach of the especially suitable catalyst for manufacture of a metal support catalyst. Then, it will describe [ a detail and ] concretely about the manufacture approach of the ultrafine particle dispersion liquid containing the metallic element used as the manufacture raw material of this catalyst. The aforementioned ultrafine particle dispersion liquid are obtained by returning the microemulsion solution containing a metal ion. Although this microemulsion is formed with the water solution and the oily liquid which dissolved the desired metal salt, it is desirable to use 1 phase system water-in-oil type microemulsion without the external aqueous phase especially in this invention. moreover, a metal salt -- water solubility -- reduction -- although it will not be limited if it is an easy salt, especially a chloride and a nitrate are desirable.

[0015] If the metal salt which said microemulsion is made to contain is illustrated concretely platinum-salts [ , such as chloroplatinate and tetra-ammine platinum salts, ]; -- palladium salt [ , such as a palladium chloride and tetra-ammine dichloro palladium, ]; -- a rhodium chloride -- A nitric-acid rhodium, Rhodium salt [ , such as a hexa ammine rhodium, ]; Ruthenium salt [ , such as ruthenium chloride and a hexa KURORU ruthenate, ]; Iridium salt [ , such as an iridium chloride and hexa KURORU iridium acid chloride, ]; Osmium salt [ , such as a chlorination osmium and a hexa KURORU osmate, ]; Gold salt [ , such as a gold chloride, ]; Copper salt [ , such as a copper chloride and a copper nitrate, ]; Iron salt [ , such as ferric chloride and iron nitrate, ]; Nickel salt [ , such as a nickel chloride and nickel nitrate, ]; Cobalt salt [ , such as a cobalt chloride and a cobalt nitrate, ]; Silver salt [ , such as a silver nitrate, ]; Molybdenum salt [ , such as a molybdenum chloride and molybdate, ]; rhenium salt [ , such as rhenium chloride and hexa KURORU rhenate, ]; -- tungsten salt [ , such as tungsten chloride and a tungstate, ]; -- chromium salt [ , such as a chromium chloride and a chromium nitrate, ]; -- it is manganese salt, such as a manganese chloride and manganese

nitrate, etc.

[0016] Although the oily liquids used for formation of said microemulsion are a cyclohexane, n-hexane, n-heptane, an isooctane, n-Deccan, benzene, a xylene, butylbenzene, a hexanol, an octanol, a cyclohexanol, dibutyl phthalate, octylic acid butyl, a methyl ethyl ketone, etc., its liquid of hypoviscosity like a cyclohexane is desirable. Moreover, the surface active agents used for microemulsion formation are the polyethylene-glycol-p-nonylphenyl ether (NP-5), pentaethylene glycol dodecylether, the G 2-ethylhexyl sulfo sodium succinate (AOT), a cetyl trimethylammonium star's picture, etc., and a nonionic surfactant and its cationic surfactant are desirable. What is necessary is just to define suitably the mixing ratio of the metal salt water solution in the case of microemulsion formation, and an oily liquid, the mixing ratio of the water contained in an emulsion, and a surfactant, and the metal salt concentration in a water solution according to the particle size for which the ultrafine particle containing the metallic element formed asks. And the ratio of an oily liquid to a metal salt water solution is [ four or more ] preferably good at a capacity factor to carry out to ten or more.

[0017] The aforementioned microemulsion has the inclination for a drop to become small, so that there are many surfactant additions, and for the ultrafine particle containing the metallic element obtained, so that there is little metal molecularity in a drop piece to become small. therefore, a surface active agent -- more than 10 mol % of the water in an emulsion -- desirable -- more than 40 mol % -- it is good to add. Moreover, it is good to make preferably 0.05 mols /or less of ten or less metal molecularity in a drop piece into two or less pieces for the metal salt concentration in a water solution as 0.02 mols/l. or less l. If the amount of a surfactant and the oily liquid used is made extensive and metal salt concentration in a water solution is made small so that the above explanation may also show, the ultrafine particle containing the metallic element formed will become small. What is necessary is just to define suitably the particle size of the ultrafine particle containing a metallic element according to the catalytic activity for which it asks. In addition, according to the experiment of this invention persons, the magnitude of the ultrafine particle containing the metallic element obtained will be 1 to 3 times the value calculated from the surfactant in an emulsion, the drop size called for from the ratio of water, and metal salt concentration. Microemulsion can be water middle oil drop type microemulsion which contains a metal salt in the microemulsion of a two phase system besides a 1 phase system water-in-oil type emulsion, and an oil.

[0018] Reduction of the metal salt in the inside of microemulsion is the easiest to carry out by the hydrazine also by the method of irradiating ultraviolet rays besides the chemical approach, and a gamma ray which uses a hydrazine, hydrogen, a sodium borohydride, etc. as a reducing agent, although it is possible. hydrazine reduction -- solution temperature -- 10-40 degrees C -- desirable -- 20-30 degrees C -- maintaining -- more than 1 mol twice of the amount of theory -- it is preferably carried out by the twice as many 2-10-mol hydrazine as this. In this case, a hydrazine is good to add the whole quantity quickly in the microemulsion which the form of one hydrate is sufficient as and is agitated. Moreover, although nitrogen is generated to reaction time in hydrazine reduction, this is escaped to a gaseous phase or underwater and does not influence consecutive alkoxide hydrolysis. In addition, although the ultrafine particle which consists of a metal and the compound of a hydrazine like a rhodium chloride at the time of hydrazine reduction may be formed, after manufacturing the catalyst which supported this ultrafine particle, in such a case, hydrogen reduction of this is carried out, and it should just change said compound into an ultrafine particle-like metal. A hydrogen reduction method is advantageous in cost among said reduction. After this approach removes the oxygen in a solution enough with inert gas, such as nitrogen, beforehand, it is performed by letting hydrogen gas pass in a solution under churning etc. In addition, although the reduction from which the most uniform ultra-fine particle is obtained is a method of irradiating ultraviolet rays and a gamma ray, by this irradiating method, equipment turns large up, and there is a difficulty in the selective surface of a solvent etc., and it is not a not much desirable approach.

[0019] According to this invention, a metallic-oxide support catalyst can be manufactured by using as a raw material the microemulsion in which the metal salt water solution exists as an ultrafine particle-like drop. The water solution of a metal salt convertible into an insoluble hydroxide is used. namely, -- if it hydrolyzes -- water -- A microemulsion solution is produced by the same approach as the time of the above mentioned ultra-fine particle dispersion-liquid manufacture. After changing this metal salt into a hydroxide by the approach of adding aqueous ammonia at a room temperature, agitating this solution well If a metal alkoxide is hydrolyzed in the dispersion liquid by which the ultrafine particle of this hydroxide is distributed and the obtained product is calcinated, the catalyst which supported the ultrafine particle-like metallic oxide will be formed. and the microemulsion solution manufacture raw material and manufacture conditions in this case -- the time of said microemulsion manufacture for ultra-fine particle dispersion-liquid manufacture raw materials carried out -- being the same . moreover, a water-soluble metal salt -- water -- pH adjustment for changing into an insoluble hydroxide -- commercial dark aqueous ammonia etc. -- it carries out -- \*\*\*\*ing -- pH -- 9-10, then water -- an insoluble hydroxide is formed. In addition, mixed use of two or more sorts of water-soluble metal salts may be carried out at the water-insoluble nature hydroxide manufacture raw material in this case, and the catalyst

which supported two or more metallic-oxide ultrafine particles in this case can be acquired. Furthermore, it is also possible to use together a water-soluble metal salt and a water-soluble nonmetal compound, and the metallic-oxide ultrafine particle support catalyst which contains nonmetals, such as Lynn and sulfur, by the using [ together ] method is acquired.

[0020] The metallic-oxide colloid which hydrolyzed the metal alkoxide in the ultrafine particle dispersion liquid which are the above, and were made and obtained, and supported the ultrafine particle with this invention is obtained, hydrogen reduction of this is calcinated or carried out if needed after desiccation / shaping, and a support catalyst is manufactured. As a metal alkoxide, the metallic oxide can be used for catalyst support, and is not limited especially that what is necessary is just a \*\*\*\* thing. For example, the silicon alkoxide which forms a silica with large surface area, and the aluminum alkoxide which forms an alumina are used preferably, and the zirconium alkoxide which forms the titanium alkoxide which forms a titania, and a zirconia can also be used. Furthermore, the metal alkoxide which gives a magnesia, boria, NIOBIA, a lanthanum trioxide, etc. is also usable. Moreover, a metal alkoxide may be independent, or two or more kinds may use, mixing, and if the metal alkoxide mixture which consists of a metal of a different kind is hydrolyzed, a multiple oxide like a silica alumina or a silica-alumina-magnesia will be obtained. In addition, since the hydrolysis rate of a metal alkoxide is greatly different by the class in many cases, it is good to add a hydrolysis catalyst, in obtaining a multiple oxide, and to make the hydrolysis rate into same extent.

[0021] In this invention, when the metal alkoxide used for the manufacture raw material of metallic-oxide colloid is illustrated concretely, it is as follows. Silicon alkoxides, such as silicon tetra-ethoxide, silicon tetra-isopropoxide, and silicon tetra-butoxide; Aluminum NIUMUTORI ethoxide, Aluminum alkoxides, such as aluminum TORIISO propoxide and aluminum tributoxide; Titanium tetra-ethoxide, Titanium alkoxides, such as titanium tetra-isopropoxide and titanium butoxide; Zirconium ethoxide, zirconium alkoxide; magnesium, such as zirconium tetra-isopropoxide and zirconium tetra-butoxide, -- a jib -- TOKISHIDO, PENTA butoxy niobium, and TORIBU -- an ibis -- a crimp run and TORIBU -- an ibis -- a silane tongue and others. What is necessary is just to use these metal alkoxides according to the class of metallic-oxide colloid for which it asks, choosing them suitably.

[0022] In the hydrolysis reaction of the metal alkoxide in the inside of ultrafine particle dispersion liquid, water required for the hydrolysis reaction of the metal alkoxide can also be made to exist in ultrafine particle dispersion liquid beforehand, and can also be added in ultrafine particle dispersion liquid on the occasion of the hydrolysis reaction of a metal alkoxide. Moreover, at the time of reaction initiation, water required for a reaction may make the whole quantity exist in ultrafine particle dispersion liquid, and may be gradually added with advance of a reaction. it uses on the occasion of the hydrolysis reaction of a metal alkoxide -- all -- the 1-10-mol twice of the amount of theory by which amount of water is needed for the hydrolysis reaction of a metal alkoxide -- it is 1-3-mol twice preferably. Depending on the class of metal alkoxide, since the hydrolysis rate is slow, use of a catalyst may be desirable. In this case, what is necessary is just to use the water containing about 0.01 - 1% of the weight of aqueous ammonia, or about 0.01 - 1% of the weight of the aqua fortis as water for hydrolysis. As a metal alkoxide with a slow hydrolysis rate, silicon tetra-ethoxide, silicon tetra-isopropoxide, etc. are mentioned.

[0023] Although hydrolysis temperature changes also with classes of metal alkoxide, generally it is 30-50 degrees C preferably 20-60 degrees C. When adding water to dispersion liquid, as for the addition water, it is desirable for 1 - 2 hours to divide preferably from reaction initiation for 0 to 8 hours, and to add. Moreover, after addition termination of water, under 1 - 8-hour stirring, it is kept desirable at 30-50 degrees C, a hydrolysis reaction is completed, and it is preferably good for it to make [ 20-60-degree C ] it ripe at said temperature preferably for 1 to 2 hours after that for 0 to 3 hours for 0 to 12 hours. In this hydrolysis reaction, a reaction progresses and a colloid product is formed. although pH of the reaction mixture of hydrolysis reaction time changes with classes of metal alkoxide etc. -- general -- 3-11 -- it is preferably good 7-11, and to be more preferably referred to as 8-10.

[0024] When making a metal alkoxide hydrolyze in ultrafine particle dispersion liquid by this invention, it is important to make the metallic oxide which avoids gel-ization (hyperviscosity-izing) of the whole dispersion liquid, and is generated by hydrolysis of a metal alkoxide exist by the shape of a colloidal particle (the shape of settlings). Gelation of the whole dispersion liquid may not accept catalytic activity in the manifestation of the catalyst effectiveness by the ultrafine particle being checked in order that a metallic oxide may cover the front face of an ultrafine particle, therefore more than 1000m<sup>2</sup>/g having BET surface area. Therefore, what is necessary is for that for an alkaline water solution just to perform the hydrolysis reaction of a metal alkoxide, although it is desirable to avoid gel-ization of the whole dispersion liquid.

[0025] Although the metallic-oxide colloid which supported the ultrafine particle as mentioned above is formed, this thing exists by the shape of a precipitation particle in a reactor, after an aging period expires. After this product carries out solid liquid separation of this and uses this precipitate as a mother liquor a \*\* exception, it can acquire a support



catalyst by alcohol etc. washing and removing impurities, such as a surfactant, heating and drying subsequently to the bottom of ordinary pressure or reduced pressure, and removing water, the oily liquid to contain. Thus, what is necessary is to calcinate it under a desired ambient atmosphere, if the metallic oxide which carried out homogeneity support of the obtained ultrafine particle is required after grinding to a desired grain size, or to fabricate it in the form of a request after processing of hydrogen reduction etc., and just to make it into a catalyst. In addition, it may dry, after processing it in the shape of a honeycomb etc., and the paste-like metallic-oxide colloid refined by alcoholic washing etc. may be used for a catalyst.

[0026] According to this invention, the metallic oxide which carried out homogeneity support of the ultrafine particle with a particle size of 5-200A at a front face or the whole is obtained. And since hydrolysis and aging of a metal alkoxide are performed at low temperature, this ultrafine particle does not carry out thermal metamorphism of them during hydrolysis. Moreover, since what is necessary is just to also perform desiccation of a product under reduced pressure of 100 degrees C or less, in this product, there are no problems, like the ultrafine particle of a raw material carries out heat condensation, and the product by which homogeneity distribution of the ultrafine particle of a raw material and the particle of the same particle size was carried out is obtained. Therefore, the support catalyst which fabricates this product and is acquired differs from the conventional alkoxide method catalyst or the conventional ultrafine particle support catalyst. That is, since the conventional alkoxide method metal support catalyst is acquired from the precursor which carried out homogeneity distribution of the metal salt into metallic-oxide gel, it has problems, like metal particle size becomes heterogeneity by heating and the chemical reaction at the time of changing a metal salt into a metal. Moreover, in case a support catalyst is manufactured from support and a water-soluble salt by the usual sinking-in method, particle size distribution and the distance between particles change greatly by the surface state of support etc., but in the case of this invention, since a catalyst is manufactured at the temperature from which the condensation between particles does not take place, the support catalyst which has the ultrafine particle of not condensing with sharp particle size distribution, on a front face can be acquired.

[0027] Since the ultrafine particle has combined independently strongly the catalyst formed as mentioned above with the metallic-oxide front face formed by hydrolysis of an alkoxide, the stability of an ultrafine particle is very good and the ultra-fine particle does not condense it under an elevated temperature with an ultra-fine particle support catalyst. Therefore, since the condensation (sintering) to which an independent particle comrade does not condense the metal which a catalyst tends to condense like copper or palladium, either, but it serves as the main factor of an activity fall does not take place, maintenance of high activity is possible over a long period of time.

[0028]

[Example] Hereafter, although an example and the example of a comparison explain this invention still more concretely, this invention is not limited in this example. In addition, the following sections and % are weight criteria.

[0029] Shortly after putting the homogeneity water solution which consists of the 2Ochloroplatinic acid 6 hydrate  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  section and the distilled water 15 section into the beaker of 300ml of example 1 content volume, adding the cyclohexane 190 section and the polyethylene-glycol nonylphenyl ether (chain length 5; nonionic surface active agent) 69 section to this and agitating with a magnetic stirrer under the room temperature, the microemulsion containing 0.14g platinum ion was formed into 100g. This microemulsion is a 1 phase system water-in-oil type, a drop diameter is calculated with an average of 22A from the amount of surfactants, and the amount of water, and the number of platinum ion contained in one drop from this value and the underwater concentration of platinum ion is calculated with an average of 0.5 pieces. The hydrazine 1 hydrate  $\text{N}_2\text{H}_4$  and 2OH0.6 commercial section was added to this microemulsion, it agitated with for [ sufficient to the bottom of a room temperature ] 30 minutes to it, and platinum ion was returned to it at the platinum ultrafine particle. Thus, the platinum particle size of the obtained platinum ultrafine particle dispersion liquid is presumed to be the diameter of about 40A from the magnitude of a drop etc.

[0030] The distilled water 10 section was added to the platinum ultrafine particle dispersion-liquid 275 aforementioned section, and after agitating well until it became homogeneity, aqueous ammonia adjusted pH of liquid to 8.5-9.5 28%. After melting the silicon tetra-ethoxide of the 67 sections well in this liquid, churning was continued with the magnetic stirrer for 2 hours, heating this at 35-40 degrees C with a water bath. Since silica colloid was formed at a hydrolysis reaction and liquid became muddy when agitated, in order to complete a hydrolysis reaction, the 20 sections of distilled water were added further, and churning was continued for 2 hours. Heating was stopped in 4 hours after reaction initiation, after cooling the contents of a beaker to the room temperature, the mother liquor was carried out the \*\* exception and the obtained precipitate was washed 3 times by the ethanol of the 200 sections. After drying this purification precipitate at 80 degrees C for 12 hours, when it calcinated at 500 degrees C under air circulation for 4 hours, the silica gel 12 section containing 3.0% of platinum was obtained, the silica gel yield from raw material silicon tetra-ethoxide was 65% of the amount of theory, and the platinum yield from chloroplatinic acid was quantitive.



Moreover, in the result of observation by the electron microscope, the particle size of the platinum support silica gel obtained here is fully uniform, and had the particle size whose all are about 0.03 micrometers.

[0031] In order to evaluate the engine performance of the 3% platinum-silica gel catalyst prepared as mentioned above, this catalyst was fabricated with the tablet shaping vessel, particle size was made into 16-24 meshes, the coil with a bore of 17mm was loaded with 2g of this molding catalyst, and the combustion reaction nature of a propane was investigated. That is, the coil was installed into the possible electric furnace of temperature control by temperature width of face of less than 1 degree C, and the mixed gas of propane:oxygen:nitrogen =0.5:10:89.5 (capacity factor) was fed into this coil the rate for 150ml/. And catalyst ability was evaluated from the propane conversion at the time of making catalyst bed temperature into 150 degrees C, 200 degrees C, and 250 degrees C. A result is shown in Table 1.

[0032] an example of comparison 1 comparison sake -- the product made from Fuji DAVISON -- the catalyst of 16-24 meshes of particle size which made silica gel Cariat-50 support 3.0% of platinum was prepared, the completely same evaluation experiment as an example 1 was conducted, and the result was written together to Table 1. In addition, the catalyst of the example 1 of a comparison is a catalyst which dried at 80 degrees C for 8 hours after using diamine nitrous-acid platinum as platinum salts of a raw material and making silica gel support said compound with a conventional method so that there may be no reaction inhibition by chlorine, returned for 2 hours and prepared this at 450 degrees C among the hydrogen air current.

[0033]

[Table 1]

	プロパンの転化率 (%)		
	150℃の反応	200℃の反応	250℃の反応
実施例 1	5	32	82
比較例 1	0	11	67

It is clearer from Table 1 than the catalyst of the example of a comparison that the catalyst's of an example it is high activity. Therefore, with the combustion catalyst of the propane which uses platinum as the catalyst matter, the catalyst prepared by the ultrafine particle distributed alkoxide method of this invention can be called high activity from the conventional platinum support catalyst.

[0034] The microemulsion in which the one section and distilled water put the homogeneity liquid which consists of the ten sections, and it contains rhodium ion 0.21g in 100g when rhodium chloride 3 monohydrate  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  adds the surface-active-agent 46 same section as the cyclohexane 127 section and the thing used in the example 1 to this and agitates with a magnetic stirrer under a room temperature was immediately formed in the beaker of 300ml of example 2 content volume. This microemulsion is a 1 phase system water-in-oil type, the diameter of a drop is calculated with 22A (average value), and the number of the rhodium ion contained in one drop is calculated with an average of 1.3 pieces. Commercial hydrazine 1 hydrate  $\text{N}_2\text{H}_4$  and  $\text{H}_2\text{O}$  were agitated with for [ sufficient to the bottom of 0.6 \*\*\*\*\* and a room temperature ] 30 minutes to this microemulsion, and rhodium ion was returned to the ultrafine particle containing a rhodium. Thus, the particle size of the rhodium content particle of the obtained rhodium content ultrafine particle dispersion liquid is presumed to be the diameter of about 30A from the magnitude of a drop, and the number of rhodium ion in a drop.

[0035] The distilled water 15 section was added to the rhodium content ultrafine particle dispersion-liquid 184 aforementioned section, and pH of liquid was set to 8.5-9.5 with aqueous ammonia 28% after churning until it became homogeneity. After melting the silicon tetra-ethoxide of the 110 sections in this liquid, churning was continued with the magnetic stirrer for 2 hours, heating this at 35-40 degrees C with a water bath. If it had agitated, since silica colloid would be formed at a hydrolysis reaction and liquid would become muddy, the 30 sections, in addition churning were further continued for ion exchange water for 2 hours, and the hydrolysis reaction was completed. Next, the precipitation obtained in the mother liquor by carrying out beaker contents a \*\* exception after cooling to a room temperature was washed 3 times by the ethanol of the 200 sections. When this purification precipitation was calcinated at 500 degrees C under air circulation after 12-hour desiccation by 80 degrees C for 4 hours and it calcinated at 450 degrees C under hydrogen circulation further for 2 hours, the silica gel 19 section with a particle size [ containing 2.0% of rhodium ] of

0.2-0.4 micrometers was obtained. The silica gel yield from raw material silicon tetra-ethoxide was 62% of the amount of theory, and the rhodium yield from a rhodium chloride was quantitative.

[0036] In order to evaluate the engine performance of the 2% rhodium-silica gel catalyst prepared as mentioned above, this catalyst was fabricated with the tablet shaping vessel, particle size was made into 16-24 meshes, and the hydrogenation reaction of the carbon monoxide which uses this molding catalyst was performed. That is, the gaseous-phase circulation reaction with a pressure of 40kg/cm<sup>2</sup> which uses a 2g catalyst using the same reactor as an example 1 was performed, it investigated about the relation between reaction temperature and reaction results, and the result of Table 2 was obtained. In addition, in this evaluation experiment, the mixed gas of carbon monoxide:hydrogen:argon =3:6:1 (mole ratio) was used for material gas, and GHSV6000/hr performed. GHSV is the abbreviation for gas space velocity, and means the material gas capacity of the reference condition which passes through the catalyst top of unit capacity in 1 hour here. Moreover, the BET surface area of the platinum-silica catalyst used in this evaluation experiment was 61m<sup>2</sup>/g.

[0037] Except having changed the silicon tetra-ethoxide addition to example 3 rhodium content ultrafine particle dispersion liquid, after producing a 4.5% rhodium-silica gel catalyst by the same approach as an example 2 and considering as the molding catalyst of 16-24 meshes of particle size by the same approach as an example 2, the result of having performed the same evaluation trial as an example 2 is shown in Table 2. This evaluation trial used the material gas of the same presentation as an example 2, and although carried out by the same pressure as an example 2, GHSV set it to 2000/hr.

[0038] an example of comparison 2 comparison sake -- the product made from Fuji DAVISON -- the catalyst of the same particle size as the example 2 which made silica gel Cariat-50 support 2.0% of rhodium with the sinking-in method was prepared, except having set GHSV to 3000/hr, the same evaluation trial as an example 2 was performed, and the result shown in Table 2 was obtained. In addition, the catalyst of this example of a comparison was produced using the same rhodium chloride as the case of an example 2, and the BET surface area of a catalyst was 60m<sup>2</sup>/g.

[0039] After setting pH of liquid to 3-4 with the nitric acid of 1 convention after churning and dissolving the silicon tetra-ethoxide of the 71 sections in this solution until it added the distilled water 15 section to the rhodium content ultrafine particle dispersion-liquid 184 section manufactured in the example of comparison 3 example 2 and became homogeneity, the hydrolysis reaction of silicon tetra-ethoxide was performed by the same approach as an example 2. However, unlike the case of an example 2, precipitate did not generate in this case, but reactor contents became a jelly-like transparency solid-state. This solid could be ground after cooling to the room temperature, it could take out from the reactor, and the same approach as the case of an example 2 could be used, and when desiccation, air baking, and hydrogen reduction were performed on the same conditions as the case of an example 2 after washing, 19 \*\*\*\*\*, the silica gel yield from silicon tetra-ethoxide, and the rhodium yield from a rhodium chloride had the almost quantitative silica gel containing 2.0% of rhodium. Moreover, the acquired catalyst was the vitrified solid-state which has a feeling of transparency a little, and was BET surface area 1020m<sup>2</sup>/g. After pulverizing this catalyst well, it fabricates by the same approach as an example 2, and except having set GHSV to 1000/hr, it is the same approach as an example 2, and the result of having performed the hydrogenation reaction of a carbon monoxide is shown in Table 2.

[0040]

[Table 2]

	反応温度 (℃)	一酸化炭素 反応率(%)	STY* (g/l·hr)	GHSV (hr <sup>-1</sup> )	BET表面積 (m <sup>2</sup> /g)
実施例 2	240	4.3	18	6000	61
	260	9.0	29.1	6000	61
	280	19.4	51.8	6000	61
実施例 3	180	5.1	16.3	2000	—
	200	20.5	60.3	2000	—
	220	58.1	248.3	2000	—
比較例 2	260	0.9	4.2	3000	60
	280	3.1	16.2	3000	60
	300	9.3	47.2	3000	60
比較例 3	240	0.6	trace	1000	1020
	280	1.5	0.2	1000	1020
	300	2.2	0.3	1000	1020

\* The value which shows the amount of generation of a with a carbon numbers of two or more generated per amount of catalysts of 1l. in 1 hour oxygenated compound (g).

[0041] Although it is clear from Table 2 that the catalyst's of an example activity is more sharply [ than the catalyst of the example of a comparison ] high, it is interesting that activity is lower than the catalyst (catalyst of the example 2 of a comparison) with which the catalyst of the example 3 of a comparison manufactured by the approach similar to the approach of this invention is manufactured by the sinking-in method. Moreover, the catalyst of the example 3 with many amounts of rhodium support is excellent in the catalyst of an example, and STY248.3 g/l-hr obtained in the experiment using this catalyst is a peak price in the data obtained by current as the with a carbon numbers [ by hydrogenation of a carbon monoxide ] of two or more oxygenated organic compound manufacture approach. In addition, it is clear from Table 2 that the activity difference's in the rhodium catalyst which hydrogenates a carbon monoxide it is not what is depended on the difference of surface area.

[0042] Taking and agitating the ammonium metavanadate 3.5 section, the distilled water 50 section, and the oxalic acid 7.46 section to the beaker of 1l. of example 4 content volume, it heated at 80 degrees C and considered as homogeneity liquid. This was made to carry out the homogeneity dissolution of the ammonium-dihydrogenphosphate 3.4 section after cooling this liquid to a room temperature, the aqua fortis of 1 convention was added to this liquid, and pH of liquid was adjusted to 3-4. In case this pH adjustment prepares microemulsion by using the aforementioned mixed liquor as a raw material, it is pH adjustment for preventing ammonium dihydrogenphosphate precipitating. When the surface-active-agent 110 same section as the cyclohexane 390 section and the thing used in the example 1 was added to the aforementioned mixed liquor and it agitated with the magnetic stirrer under the room temperature (25 degrees C), the microemulsion which contains Lynn 0.16g and vanadium 0.26g in 100g generated immediately. This microemulsion is a 1 phase system water-in-oil type, and since the average diameter of a drop is calculated with 45A, both the atomic number of Lynn included in each drop and vanadium is calculated with an average of 11 pieces. Aqueous ammonia was added to this microemulsion 28%, pH was set to 9-9.5, and the ultrafine particle dispersion liquid which agitate for 30 minutes at a room temperature, and contain Lynn and vanadium were produced.

[0043] The distilled water 5 section could be added to said dispersion-liquid 190 section, and it agitated, and pH dissolved the silicon tetra-ethoxide 60 section in the dispersion liquid diluted with the aforementioned water currently kept at 9-9.5, and agitated this liquid at 40-45 degrees C for 2 hours. Consequently, since silicon tetra-ethoxide was hydrolyzed and silica colloid precipitate generated, in order to complete a hydrolysis reaction, 30 \*\*\*\*\* and 2 more hour churning were continued for distilled water which adjusted pH to 9 with aqueous ammonia. After reaction termination, after cooling the product to the room temperature, the surfactant and organic solvent which carry out a mother liquor a \*\* exception, wash the obtained precipitate 3 times by the ethanol of the 200 sections, and are contained

in precipitate were fully removed. After drying this precipitate at 80 degrees C for 12 hours, when it calcinated at 500 degrees C under air circulation for 4 hours, the silica gel 11 section containing 11% of VOPO<sub>4</sub> was obtained. The silica gel yield from raw material silicon tetra-ethoxide was about 60% of the amount of theory, and the yield of V and P from ammonium metavanadate and ammonium dihydrogenphosphate was about 90% of the amount of theory. In addition, the BET surface area of the generated VOPO<sub>4</sub> support silica gel was 38m<sup>2</sup>/g.

[0044] In order to evaluate the engine performance of the 11%VOPO<sub>4</sub>-silica gel catalyst prepared by the above-mentioned approach, this catalyst was fabricated with the tablet shaping vessel, particle size was made into 16-24 meshes, the coil (the same object as what was used in the example 1) with a bore of 17mm was loaded with 3g of this shaping catalyst, and the air-oxidation property of an isobutane was investigated. That is, the coil was installed in the same electric furnace as what was used in the example 1, the mixed gas of isobutane:oxygen:helium =1:1:3 (capacity factor) was fed into this coil the rate for 60ml/, it was asked for the relation between catalyst bed temperature (reaction temperature) and conversion, the relation between catalyst bed temperature and [methacrolein (MAL) + methacrylic-acid (MAA)] selectivity, etc., and the result of Table 3 was obtained to it. In addition, analysis of a resultant was performed by gas chromatography.

[0045] For the example of comparison 3 comparison, 3g of 11%VOPO<sub>4</sub>-silica gel catalysts of the sinking-in method manufactured with the conventional method was used, isobutane oxidation was performed on the same conditions as an example 4, and the result written together to Table 3 was obtained. After the catalyst used in this example of a comparison makes support the same silica gel as what was used in the example 1 of a comparison and makes this support an ammonium vanadate and ammonium dihydrogenphosphate with a conventional method, it is calcinated and prepared under circulation of air and is a catalyst of BET surface area of 61.0m<sup>2</sup>/g.

[0046] Pyrophosphoric-acid vanadyl 3g which prepared by carrying out vanadium pentoxide, hydroxylamine hydrochloride, and a phosphoric acid in the start raw material according to the approach indicated by reference [J.SHIMODA and Bull.Chem.Soc.Jpn.582163-2171 (1985)] as example of a comparison with the another example 3 of example of comparison 4 comparison is made into a catalyst, and the experimental result which oxidized the isobutane by the same approach as the case of an example 4 is shown in Table 3.

[0047]

[Table 3]

	反応温度 (℃)	反応率 (%)	反応生成物の選択率 (mol %)		
			MAL + MAA	酸化生成物*	CO + CO <sub>2</sub>
実施例 4	350	0.6	75.7	9.1	15.2
	400	2.0	61.2	8.3	28.0
	450	5.1	44.8	8.6	43.4
比較例 3	300	3.2	3.5	10.4	84.0
	350	21.1	1.0	6.5	91.4
	400	21.7	1.4	7.8	89.2
比較例 4	300	0.5	45.9	12.9	41.2
	350	3.2	18.1	16.7	62.9
	400	11.5	8.1	11.8	78.0

\* With the oxidation resultant except MAL+MAA and CO+CO<sub>2</sub>, the maleic anhydride and the oxidation product of C<sub>3</sub> are included.

[0048] From Table 3, the catalyst of this invention is understood that selectivity is more sharply [ than that of the example of a comparison ] (MAL+MAA) high. As a catalyst with partial oxidation activity high among the conventional catalysts for isobutane oxidation At the time of use of the catalyst indicated for the example 4 of a comparison which attracts attention, selectivity shows [ selectivity (MAL+MAA) ] 61.2-mol % at 0.6% of conversion at 75.7-mol % and 2.0% of conversion by the result of the example 4 for which selectivity (MAL+MAA) uses the catalyst

of this invention at 0.5% of conversion although selectivity is 18.1-mol % in 45.9-mol % and 3.2% of conversion (MAL+MAA) (MAL+MAA). Moreover, the catalyst of this invention can be called complete oxidation control mold catalyst, and even 5.1% even of conversion is known by that selectivity is only 43.4-mol % (CO+CO<sub>2</sub>) by the experimental result of the example 4 which uses the catalyst of this invention although selectivity (CO+CO<sub>2</sub>) serves as a mol 84.0% at 3.2% of conversion at the time of catalyst use of the example 3 of a comparison prepared by the usual sinking-in method.

[0049]

[Effect of the Invention] From being manufactured by the approach of hydrolyzing a metal alkoxide in the dispersion liquid which carried out homogeneity distribution of the ultrafine particle, and being hard to condense this ultrafine particle with heating etc., the support catalyst manufactured by the approach of this invention is highly efficient, and is a support catalyst with little degradation in use. Therefore, this catalyst is longer lasting than the support catalyst manufactured with a conventional method by high efficiency.

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(54) 【発明の名称】 担持触媒の製造方法

(57) 【要約】

【目的】 触媒物質の担持量と無関係に触媒物質の粒径を設定できる上に、均質で触媒製造の途中で触媒粒径が変化したりせず、長寿命で高活性な金属酸化物を担体とする触媒を提供すること。

【構成】 触媒活性を有する超微粒子の分散液中で、担体原料となる金属アルコキシドを攪拌下に水の存在下で加水分解し、コロイド状の金属酸化物粒子を生成させる工程を含むことを特徴とする担持触媒の製造方法。超微粒子の分散液が、水溶性金属化合物を含む水溶液が超微粒子状の液滴として存在するマイクロエマルジョンを原料とし、該液滴中に含まれている水溶性金属化合物を不溶化して作られたものであることを特徴とする前記担持触媒の製造方法。水溶性金属化合物の不溶化が還元反応によるものであることを特徴とする前記担持触媒の製造方法。

## 【特許請求の範囲】

【請求項1】 触媒活性を有する超微粒子の分散液中で、担体原料となる金属アルコキシドを攪拌下に水の存在下で加水分解し、コロイド状の金属酸化物粒子を生成させる工程を含むことを特徴とする担持触媒の製造方法。

【請求項2】 超微粒子の分散液が、水溶性金属化合物を含む水溶液が超微粒子状の液滴として存在するマイクロエマルジョンを原料とし、該液滴中に含まれている水溶性金属化合物を不溶化して作られたものであることを特徴とする請求項1に記載した担持触媒の製造方法。

【請求項3】 水溶性金属化合物の不溶化が還元反応によるものであることを特徴とする請求項2に記載した担持触媒の製造方法。

## 【発明の詳細な説明】

## 【0001】

【産業上に利用分野】本発明は、金属等の触媒活性を有する超微粒子を分散した担持触媒の製造方法に関するものである。

## 【0002】

【従来の技術】周知のように、不均一触媒を使用する接触反応では触媒表面で反応が進行するから、この方面の研究者は試行錯誤的に表面活性の大きい触媒を探索している。この場合、単位表面積当りの活性物質の量及び質が同じなら表面積が広いほど活性が高くなるので、触媒物質の担体には表面積の大きいシリカやアルミナのような無機酸化物ゲルを使う場合が多い。そして、前記無機酸化物ゲルの一般的製造方法は、無機塩の加水分解で得られた無機酸化物ゲルを焼成・脱水する方法であるが、この方法では原料塩や加水分解試薬に由来するナトリウム等の無機イオンが不可避免的に微量混入し、これが触媒の活性や物性に影響を及ぼす場合も少なくない。また、前記の方法で得られた無機酸化物ゲルに含浸法で触媒物質を担持させる場合が多いが、該方法で表面の均質な触媒を得るのは至難である。さらに、従来法では金属担持量で触媒金属の粒径が定まってしまうような問題もあり、金属担持量と無関係に粒径を設定できる技術が求められている。

【0003】前記した表面の不均質が不均一触媒の理論的探索を困難にしており、これが触媒開発や触媒理論の発展を妨げているから、均質で高活性な触媒の開発が昔から触媒研究者の課題であった。しかも、分析技術の発展で均質と思われていた触媒表面の多くが不均質なことも分り、該触媒の開発は進んでいない。この一因は、触媒物質を含浸法で担体に担持する際に溶液から析出する触媒物質の結晶が、担体表面の細孔形状や大きさ及び結晶析出条件で大きく変るためと云われる。10年位前から、均質な触媒の調製方法としてアルコキシド法が注目されている。この方法による金属担持触媒の製造は、グリコール等の配位能を持つ親水性有機溶媒に金属塩を溶

解し、該溶液にアルミニウムやケイ素等の金属の可溶性アルコキシドを加えて均一液としてから、該アルコキシドを加水分解・熟成して対応する金属酸化物コロイドに変え、該生成物を乾燥・焼成後に水素還元することで行われる。該方法では金属酸化物コロイドの乾燥・焼成で形成されたゲルが担体となり、これに金属塩の水素還元で得られた金属が担持されて触媒となる。

【0004】アルコキシド法による金属担持触媒は、研究の進展に伴って多数の特許や報文が発表されている。例えば、特公昭60-59215号公報にはルテニウムと銅を担持したアルコキシド法シリカ触媒によるベンゼンの部分水素化法が、特公昭63-45620号公報には各種の金属担持アルコキシド法シリカ触媒が、特公昭63-45621号公報には各種の金属担持アルコキシド法アルミナ触媒が、特公昭63-45622号公報には各種の金属担持アルコキシド法チタニア触媒が、特公昭63-45623号公報には各種の金属担持アルコキシド法ジルコニア触媒が開示されている。また、上野らはJ. Chem. Soc. Faraday Trans. 1 79 127 (1983)等に、水上らはJ. Chem. Tech. Biotechnol. 36 236 (1986)等にアルコキシド法触媒に関する研究報告を発表している。

【0005】前記のように金属担持アルコキシド法触媒は多数発表されているが、該触媒は金属塩溶液に金属アルコキシドを溶解してから、該アルコキシドを加水分解して調製されるので、金属塩を金属に転換する還元工程が必要である。この還元工程は、金属酸化物中に分散している金属塩を100℃以上で水素還元する等の高温工程が必要な上に、アルコキシドの加水分解・乾燥で得られた粒子中の金属塩は、アルコキシドの加水分解で生成した金属酸化物ゲルに吸着したり、該金属酸化物ゲルが保有する構造水中に溶解した状態等で存在するから、還元工程で形成される金属超微粒子が不均質になることが避けられない。すなわち、アルコキシド法で充分均質な金属塩の分散体を形成させても、金属塩を金属に還元する過程で金属粒径が不均質になってしまう。また、金属塩は一般に金属より化学的活性が強いから、担体となる金属酸化物と金属塩との間に結合が形成される場合もあり、そのために金属塩の還元で触媒活性を持つ金属を形成させた場合に、該金属固有の性質が損なわれたり、異質の活性が付加されたりする場合もある。

【0006】一方、超微粒子製造法もコロイド化学の分野等で以前から研究されており、例えば最近急速に進歩しているマイクロエマルジョンを原料とする方法では、直径数Å～数10Åの金属超微粒子や金属化合物超微粒子の作製例が発表されている〔USP 4,425,261 (1984); Colloids Surface 5 209 (1982)等〕。該方法は、超微粒子原料の金属塩水溶液と界面活性剤と油から、油中に所望量



の金属塩を含む所望の大きさの液滴を形成させ、該金属塩をヒドラジンや水素等で還元して金属超微粒子を得る方法である。金属超微粒子は今後の機能材料として期待されており、我が国でもその製造方法等が国家プロジェクトとして検討され、金属蒸気から金属超微粒子を得る方法等が発表されている。また、超微粒子の製造方法や物性等については化学総説No. 48（日本化学会編、1985年発行）に詳記されている。

【0007】

【発明が解決しようとする課題】本発明は、従来のアルコキシド法による触媒の製造方法に見られる前記の諸問題を解決し、超微粒子が担持されている触媒性能に優れた担持触媒の製造方法を提供することをその課題とする。

【0008】

【課題を解決するための手段】本発明者らは、前記課題を解決すべく鋭意研究を重ねた結果、本発明を完成するに至った。すなわち、本発明によれば、触媒活性を有する超微粒子の分散液中で、担体原料となる金属アルコキシドを攪拌下に水の存在下で加水分解し、コロイド状金属酸化物粒子を生成させる工程を含むことを特徴とする担持触媒の製造方法が提供される。また、本発明によれば、超微粒子の分散液が水溶性金属化合物を含む水溶液が超微粒子状の液滴として存在するマイクロエマルジョンを原料とし、該液滴中に含まれている水溶性金属化合物を不溶化して作られたものであることを特徴とする前記の担持触媒の製造方法が提供される。さらに、本発明によれば、水溶性金属化合物の不溶化が還元反応によるものであることを特徴とする前記の担持触媒の製造方法が提供される。

【0009】本発明において、担持触媒の調製原料となる超微粒子分散液は、触媒活性を持つ超微粒子を分散媒に均一分散した液である。分散媒となる液体は、分散させる超微粒子と反応したり該粒子を溶解したりせず、使用する金属アルコキシドを溶解し得る有機溶媒、又は該溶媒と水との混合液が使われる。また、該分散液には超微粒子を安定に分散させるために、界面活性剤を分散液重量の0.5～40%、好ましくは4～20%含有させることができる。分散液中の超微粒子含有率は、一般に0.0001～3重量%、好ましくは0.1～1重量%である。また、分散液は所定量の超微粒子と分散媒と界面活性剤とを混合し、ジェットミルやボールミル等の強力な分散機を用いて分散媒中に超微粒子を分散させることによって得ることができる。

【0010】触媒活性を有する超微粒子としては、触媒能を持つものであればどのようなものでもよく、このようなものには、遷移金属、特に、V族～VIII族の遷移金属の中から選ばれる金属、金属酸化物や金属硫化物等の金属化合物、或いは不溶性金属塩等の種々の超微粒子を使うことができる。また、前記の超微粒子は単独でも二

種以上混合して使っても良く、二種以上混合使用の例としては、超微粒子状銅と超微粒子状ルテニウムの混合物を含有するベンゼンの部分水素化触媒の例等が挙げられる。

【0011】本発明で使われる超微粒子は、①水溶性化合物を含むマイクロエマルジョンを還元処理や酸化処理する方法、②蒸気を急冷する方法、③気相熱分解や気相酸化等の気相反応で形成させる方法、等の種々の方法で製造することができる。前記製造方法のうち、②及び③の方法で得られた超微粒子は、これを分散媒に分散させることによって分散液を得ることができる。一方、①の方法では超微粒子分散液の形態で超微粒子が得られるから、これをそのまま本発明で用いる超微粒子含有分散液として使うことができるし、必要に応じて有機溶媒や水を加えて本発明の超微粒子含有分散液として使うことも可能である。

【0012】超微粒子分散液の分散媒となる有機溶媒を例示すると、シクロヘキサン、シクロヘプタン、n-ヘキサン、n-ヘプタン、イソオクタン、n-デカン、ベンゼン、キシレン等の炭化水素；ヘキサノール、ヘプタノール、オクタノール等の比較的長鎖の脂肪族一価アルコール；アセトン、メチルエチルケトン等の脂肪族ケトン；等が挙げられる。これらの溶媒は、単独でも混合して使っても良い。超微粒子分散液に用いられる界面活性剤は特に限定されず、陽イオン性、陰イオン性、非イオン性及び両性の界面活性剤を用いることができる。その具体例としては、ポリエチレングリコール-p-ノニルフェニルエーテル、ペンタエチレングリコールドデシルエーテル、ジ-2-エチルヘキシルスルホコハク酸ナトリウム、セチルトリメチルアンモニウムブロマイド等が例示される。

【0013】本発明で製造される担持触媒は、金属や金属酸化物等の触媒活性を有する超微粒子を、金属アルコキシドの加水分解で得られる金属酸化物コロイド粒子に担持させた触媒である。また、該触媒は広範囲にわたる接触反応の分野で従来法で製造される触媒より高性能な触媒である。例えば、アルカンの酸化で部分酸化生成物を製造する際に使われるバナジウム、リン及び酸素を含有する担持触媒では、従来法で製造される触媒より大幅に選択性が高い触媒を製造することができる。また、一酸化炭素の部分水素化で炭素数2以上の化合物を製造する際に使われるロジウム触媒の場合も、従来法で製造される触媒より大幅に選択性が高い触媒を製造することができる。さらに、炭化水素の完全酸化用白金触媒では従来法で製造される触媒より大幅に高活性の触媒を製造することができるから、今後の発展が期待されている燃焼触媒の製造に好適な触媒の製造方法である。

【0014】前記のように、本発明では多岐にわたる接触反応の分野で、従来法より高選択性又は高活性な上に長寿命な触媒を提供できるから、触媒製造原料が高価な

貴金属担持触媒等の製造方法として好ましい方法である。また、本発明で製造される触媒の大部分は金属元素を含む触媒であり、特に金属担持触媒の製造に好適な触媒の製造方法である。そこで、該触媒の製造原料となる金属元素を含む超微粒子分散液の製造方法について、詳細かつ具体的に記述することにする。前記の超微粒子分散液は、金属イオンを含むマイクロエマルジョン溶液を還元することで得られる。このマイクロエマルジョンは、所望の金属塩を溶解した水溶液と油性液体で形成されるが、本発明では特に外部水相のない一相系油中水滴型マイクロエマルジョンを使うのが望ましい。また、金属塩は水溶性で還元容易な塩であれば限定されないが、特に塩化物や硝酸塩が好ましい。

【0015】前記マイクロエマルジョンに含有させる金属塩を具体的に例示すると、塩化白金酸塩やテトラアンミン白金塩等の白金塩；塩化パラジウムやテトラアンミンジクロロパラジウム等のパラジウム塩；塩化ロジウム、硝酸ロジウム、ヘキサアンミンロジウム等のロジウム塩；塩化ルテニウムやヘキサクロルルテニウム酸塩等のルテニウム塩；塩化イリジウムやヘキサクロルイリジウム酸塩等のイリジウム塩；塩化オスミウムやヘキサクロルオスミウム酸塩等のオスミウム塩；塩化金等の金塩；塩化銅や硝酸銅等の銅塩；塩化鉄や硝酸鉄等の鉄塩；塩化ニッケルや硝酸ニッケル等のニッケル塩；塩化コバルトや硝酸コバルト等のコバルト塩；硝酸銀等の銀塩；塩化モリブデンやモリブデン酸塩等のモリブデン塩；塩化レニウムやヘキサクロルレニウム酸塩等のレニウム塩；塩化タングステンやタングステン酸塩等のタングステン塩；塩化クロムや硝酸クロム等のクロム塩；塩化マンガンや硝酸マンガン等のマンガン塩等である。

【0016】前記マイクロエマルジョンの形成に用いられる油性液体は、シクロヘキサン、*n*-ヘキサン、*n*-ヘプタン、イソオクタン、*n*-デカン、ベンゼン、キシレン、ブチルベンゼン、ヘキサノール、オクタノール、シクロヘキサノール、ジブチルフタレート、オクチル酸ブチル、メチルエチルケトン等であるが、シクロヘキサンのような低粘度の液体が好ましい。また、マイクロエマルジョン形成に使われる界面活性剤は、ポリエチレングリコール-*p*-ノニルフェニルエーテル（NP-5）、ペンタエチレングリコールデシルエーテル、ジ-2-エチルヘキシルスルホコハク酸ナトリウム（AOT）、セチルトリメチルアンモニウムブロマイド等であり、非イオン性界面活性剤や陽イオン性界面活性剤が望ましい。マイクロエマルジョン形成の際の金属塩水溶液と油性液体の混合比、エマルジョン中に含まれる水と界面活性剤の混合比及び水溶液中の金属塩濃度は、形成される金属元素を含む超微粒子に所望される粒径に応じて適当に定めればよい。そして、金属塩水溶液に対する油性液体の比は、容量比で4以上、好ましくは10以上とするのが良い。

【0017】前記のマイクロエマルジョンは、界面活性剤添加量が多いほど液滴が小さくなり、液滴一個内の金属分子数が少ないほど得られる金属元素を含む超微粒子が小さくなる傾向がある。従って、界面活性剤はエマルジョン中の水の10モル%以上、好ましくは40モル%以上添加するのが良い。また、水溶液中の金属塩濃度を0.05モル/リットル以下、好ましくは0.02モル/リットル以下として液滴一個内の金属分子数を10個以下、好ましくは2個以下にするのが良い。以上の説明からも分るように、界面活性剤及び油性液体の使用量を大量にして水溶液中の金属塩濃度を小さくすれば、形成される金属元素を含む超微粒子は小さくなる。金属元素を含む超微粒子の粒径は、所望する触媒活性に応じて適宜定めれば良い。なお、本発明者らの実験によると、得られる金属元素を含む超微粒子の大きさは、エマルジョン中の界面活性剤と水の比から求められる液滴サイズと金属塩濃度から計算される値の1~3倍になる。マイクロエマルジョンは、一相系油中水滴型エマルジョンの他、二相系のマイクロエマルジョンや、油中に金属塩を含む水中油滴型マイクロエマルジョンであることができる。

【0018】マイクロエマルジョン中での金属塩の還元は、ヒドラジン、水素、水素化ホウ素ナトリウム等を還元剤とする化学的方法のほか、紫外線やγ線の照射法でも可能であるが、ヒドラジンで行うのが最も容易である。ヒドラジン還元は、液温を10~40℃、好ましくは20~30℃に保ち、理論量の1モル倍以上、好ましくは2~10モル倍のヒドラジンで行われる。この場合、ヒドラジンは1水和物の形で良く攪拌されているマイクロエマルジョン中に全量を迅速に添加するのが良い。また、ヒドラジン還元では反応時に窒素を生成するが、これは気相や水中に逃散して後続のアルコキシ加水分解に影響することはない。なお、塩化ロジウムのようにヒドラジン還元時に金属とヒドラジンの化合物から成る超微粒子を形成する場合もあるが、このような場合は該超微粒子を担持した触媒を製造してから、これを水素還元して前記化合物を超微粒子状金属に変えれば良い。前記還元法のうちコスト的に有利なのは水素還元法である。この方法は、あらかじめ溶液中の酸素を窒素等の不活性ガスで充分除いてから、攪拌下に水素ガスを溶液中に通す等の方法で行われる。なお、最も均一な金属超微粒子が得られる還元法は紫外線やγ線の照射法であるが、この照射法では装置が大きくなる上に溶媒の選択面等にも難点があり、余り好ましい方法ではない。

【0019】本発明によれば、金属塩水溶液が超微粒子状の液滴として存在しているマイクロエマルジョンを原料として、金属酸化物担持触媒を製造することができる。すなわち、加水分解すると水不溶の水酸化物に転換することができる金属塩の水溶液を使って、前記した金属超微粒子分散液製造時と同じ方法でマイクロエマルジ

ョン溶液を作製し、該溶液を良く攪拌しながら室温でアンモニア水を添加する等の方法で該金属塩を水酸化物に変えてから、該水酸化物の超微粒子が分散されている分散液中で金属アルコキシドを加水分解し、得られた生成物を焼成すれば超微粒子状の金属酸化物を担持した触媒が形成される。そして、この場合のマイクロエマルジョン溶液製造原料及び製造条件は、前記した金属超微粒子分散液製造原料用のマイクロエマルジョン製造時と同じで良い。また、水溶性金属塩を水不溶の水酸化物に変えるためのpH調整は市販濃アンモニア水等で行えば良

く、pHを9~10とすれば水不溶の水酸化物が形成される。なお、この場合の水不溶性水酸化物製造原料に2種以上の水溶性金属塩を混合使用しても良く、この場合は複数の金属酸化物超微粒子を担持した触媒を得ることができる。さらに、水溶性金属塩と水溶性非金属化合物を併用することも可能であり、併用法によってリンや硫黄等の非金属を含有する金属酸化物超微粒子担持触媒が得られる。

【0020】本発明では、前記のようにして得られた超微粒子分散液中で金属アルコキシドを加水分解して超微粒子を担持した金属酸化物コロイドを得、これを乾燥・成形後に必要に応じて焼成したり水素還元したりして担持触媒を製造する。金属アルコキシドとしては、その金属酸化物が触媒担体に使われるものであればよく、特に限定されない。例えば、表面積が大きいシリカを形成するシリコンアルコキシドや、アルミナを形成するアルミニウムアルコキシドが好ましく使われるし、チタニアを形成するチタニウムアルコキシドやジルコニアを形成するジルコニウムアルコキシドも使える。さらに、マグネシア、ボリア、ニオブ、酸化ランタン等を与える金属アルコキシドも使用可能である。また、金属アルコキシドは単独でも2種類以上混合して使っても良く、異種の金属から成る金属アルコキシド混合物を加水分解すると、シリカ-アルミナやシリカ-アルミナ-マグネシアのような複合酸化物が得られる。なお、金属アルコキシドの加水分解速度はその種類で大きく違う場合が多いから、複合酸化物を得る場合には加水分解触媒を添加し、その加水分解速度を同一程度にするのがよい。

【0021】本発明において、金属酸化物コロイドの製造原料に使われる金属アルコキシドを具体的に例示すると以下のとおりである。シリコンテトラエトキシド、シリコンテトライソプロポキシド、シリコンテトラブトキシド等のシリコンアルコキシド；アルミニウムトリエトキシド、アルミニウムトリイソプロポキシド、アルミニウムトリブトキシド等のアルミニウムアルコキシド；チタニウムテトラエトキシド、チタニウムテトライソプロポキシド、チタニウムブトキシド等のチタニウムアルコキシド；ジルコニウムエトキシド、ジルコニウムテトライソプロポキシド、ジルコニウムテトラブトキシド等のジルコニウムアルコキシド；マグネシウムジブトキシ

ド、ペンタブトキシニオブ、トリブトキシボラン、トリブトキシランタンその他。これらの金属アルコキシドは、所望する金属酸化物コロイドの種類によって適宜選択して使えば良い。

【0022】超微粒子分散液中での金属アルコキシドの加水分解反応において、その金属アルコキシドの加水分解反応に必要な水は、あらかじめ超微粒子分散液中に存在させておくこともできるし、金属アルコキシドの加水分解反応に際し、超微粒子分散液中に添加することもできる。また、反応に必要な水は、反応開始時に、その全量を超微粒子分散液中に存在させても良いし、反応の進行と共に徐々に加えてもよい。金属アルコキシドの加水分解反応に際して用いる全水量は、金属アルコキシドの加水分解反応に必要とされる理論量の1~10モル倍、好ましくは1~3モル倍である。金属アルコキシドの種類によっては加水分解速度が遅いため、触媒の使用が好ましい場合もある。この場合は、加水分解用の水として、0.01~1重量%程度のアンモニア水や0.01~1重量%程度の希硝酸を含む水を用いればよい。加水分解速度が遅い金属アルコキシドとしては、シリコンテトラエトキシドやシリコンテトライソプロポキシド等が挙げられる。

【0023】加水分解温度は、金属アルコキシドの種類によっても異なるが一般に20~60℃、好ましくは30~50℃である。分散液に水を加える場合、その添加水は反応開始から0~8時間、好ましくは1~2時間の間に分割して加えるのが望ましい。また、水の添加終了後0~12時間、好ましくは1~8時間攪拌下に20~60℃、好ましくは30~50℃に保って加水分解反応を完結させ、その後0~3時間、好ましくは1~2時間前記温度で熟成させるのが良い。この加水分解反応においては、反応が進んでコロイド状生成物が形成される。加水分解反応時の反応液のpHは、金属アルコキシドの種類等によっても異なるが、一般的には3~11、好ましくは7~11、より好ましくは8~10とするのが良い。

【0024】本発明により、超微粒子分散液中で金属アルコキシドを加水分解させる場合、分散液全体のゲル状化（高粘度化）を回避し、金属アルコキシドの加水分解により生成する金属酸化物をコロイド粒子状（沈澱物状）で存在させることが重要である。分散液全体がゲル化すると、超微粒子の表面を金属酸化物が覆ってしまうために超微粒子による触媒効果の発現が阻害され、そのためにBET表面積が1000m<sup>2</sup>/g以上もあるのに触媒活性が認められない場合もある。従って、分散液全体のゲル状化を回避するのが好ましいが、このためには金属アルコキシドの加水分解反応をアルカリ性水溶液で行えば良い。

【0025】以上のようにして超微粒子を担持した金属酸化物コロイドが形成されるが、このものは、熟成期間

が終了すると反応器内に沈殿粒子状で存在する。この生成物は、これを固液分離して該沈殿を母液と濾別してから、アルコール等で洗浄して界面活性剤等の不純物を除き、次いで常圧又は減圧下に加熱・乾燥して水や含有する油性液体等を除くことにより担持触媒を得ることができる。このようにして得られた超微粒子を均一担持した金属酸化物は、所望の粒度に粉碎後に必要であれば所望の雰囲気下に焼成し、或いは水素還元等の処理後に所望の形に成形して触媒とすれば良い。なお、アルコール洗浄等で精製したペースト状の金属酸化物コロイドを、ハニカム状等に加工してから乾燥して触媒に使用しても良い。

【0026】本発明によれば、粒径5～200Åの超微粒子を表面又は全体に均一担持した金属酸化物が得られる。そして、金属アルコキシドの加水分解や熱成は低温で行われるから、加水分解中に該超微粒子が熱変質することはない。また、生成物の乾燥も100℃以下の減圧下で行えば良いから、該生成物では原料の超微粒子が熱凝集する等の問題がなく、原料の超微粒子と同一粒径の粒子が均質分散された生成物が得られる。従って、該生成物を成形して得られる担持触媒は従来のアルコキシド法触媒や従来の超微粒子担持触媒と異なっている。すなわち、従来のアルコキシド法金属担持触媒は金属塩を金属酸化物ゲル中に均一分散した前駆体から得られるから、金属塩を金属に変える際の加熱や化学反応で金属粒径が不均質になる等の問題がある。また、通常の含浸法で担体と水溶性塩から担持触媒を製造する際には、担体の表面状態等で粒径分布や粒子間距離が大きく変るが、本発明の場合は触媒が粒子間凝集の起らない温度で製造されるから、シャープな粒径分布を持った非凝集の超微粒子を表面に有する担持触媒を得ることができる。

【0027】以上のようにして形成された触媒は、アルコキシドの加水分解で形成された金属酸化物表面に超微粒子が独立して強く結合しているために、超微粒子の安定性は非常に良く、金属超微粒子担持触媒ではその金属超微粒子が高温下でも凝集しない。従って、触媒が銅やパラジウムのように凝集し易い金属でも独立粒子同志が凝集せず、活性低下の主因となる凝集（シンタリング）が起こらないために長期間にわたって高い活性の維持が可能である。

【0028】

【実施例】以下、本発明を実施例及び比較例で更に具体的に説明するが、本発明はこの実施例で限定されるものではない。なお、以下の部及び%は重量基準である。

【0029】実施例1

内容積300mlのビーカーに、塩化白金酸6水和物 $H_2PtCl_6 \cdot 6H_2O$ 1部と蒸留水15部より成る均一水溶液を入れ、これにシクロヘキサノール190部とポリエチレングリコールノニルフェニルエーテル（鎖長5；非イオン界面活性剤）69部を加え、室温下にマグネッ

クスターラーで攪拌すると、100g中に0.14gの白金イオンを含むマイクロエマルジョンがすぐに形成された。該マイクロエマルジョンは一相系油中水滴型であり、界面活性剤量と水の量から液滴直径は平均22Åと計算され、この値と白金イオンの水中濃度から液滴1個中に含まれる白金イオン数は平均0.5個と計算される。このマイクロエマルジョンに、市販のヒドラジン1水和物 $N_2H_4 \cdot H_2O$  6部を加え、室温下に30分間良く攪拌して白金イオンを白金超微粒子に還元した。このようにして得られた白金超微粒子分散液の白金粒径は、液滴の大きさ等から直径約40Å程度と推定される。

【0030】前記の白金超微粒子分散液275部に蒸留水10部を加え、均一になるまで良く攪拌してから28%アンモニア水で液のpHを8.5～9.5に調整した。この液に67部のシリコンテトラエトキシドを良く溶かしてから、これを湯浴で35～40℃に加熱しながら2時間マグネチックスターラーで攪拌を続けた。攪拌していると、加水分解反応でシリカコロイドが形成されるために液が濁ってくるから、加水分解反応を完結させるために更に蒸留水を20部添加して攪拌を2時間続けた。反応開始後4時間で加熱を中止し、ピーカーの内容物を室温まで冷却してから母液を濾別し、得られた沈殿を200部のエタノールで3回洗浄した。この精製沈殿を80℃で12時間乾燥してから、空気流通下に500℃で4時間焼成すると、3.0%の白金を含むシリカゲル12部が得られ、原料シリコンテトラエトキシドからのシリカゲル収率は理論量の65%で、塩化白金酸からの白金収量は定量的であった。また、ここに得られた白金担持シリカゲルの粒径は、電子顕微鏡による観察の結果では十分に均一であり、全部がほぼ0.03μmの粒径を持っていた。

【0031】以上のようにして調製した3%白金-シリカゲル触媒の性能を評価するため、該触媒を錠剤成形器で成形して粒径を16～24メッシュとし、この成型触媒2gを内径17mmの反応管に装填してプロパンの燃焼反応性を調べた。すなわち、温度幅1℃以内で温度制御の可能な電気炉中に反応管を設置し、この反応管にプロパン：酸素：窒素=0.5：10：89.5（容量比）の混合ガスを150ml/分の速度で送入した。そして、触媒層温度を150℃、200℃、及び250℃とした場合のプロパン反応率から触媒能を評価した。結果を表1に示す。

【0032】比較例1

比較のために、富士ダヴィソン社製シリカゲルCaria-50に3.0%の白金を担持させた粒径16～24メッシュの触媒を調製し、実施例1と全く同じ評価実験を行い、その結果を表1に併記した。なお、比較例1の触媒は塩素による反応阻害が無いように、原料の白金塩としてジアミン亜硝酸白金を使用し、常法によって

前記化合物をシリカゲルに担持させてから80℃で8時間乾燥し、これを水素気流中450℃で2時間還元して調製した触媒である。

\*【0033】

【表1】

\*

	プロパンの転化率(%)		
	150℃の反応	200℃の反応	250℃の反応
実施例1	5	32	82
比較例1	0	11	67

表1から、実施例の触媒は比較例の触媒より高活性なことが明らかである。従って、白金を触媒物質とするプロパンの燃焼触媒では、本発明の超微粒子分散型アルコキシド法で調製した触媒は従来の白金担持触媒より高活性と云える。

#### 【0034】実施例2

内容積300mlのビーカーに、塩化ロジウム3水塩RhCl<sub>3</sub>・3H<sub>2</sub>Oが1部と蒸留水が10部より成る均一液を入れ、これにシクロヘキサン127部と実施例1で使用したものと同一界面活性剤46部を加え、室温下にマグネチックスターラーで攪拌すると、100g中にロジウムイオン0.21gを含むマイクロエマルジョンがすぐに形成された。該マイクロエマルジョンは一相系油中水滴型であり、液滴の直径は22Å(平均値)と計算され、一つの液滴中に含まれるロジウムイオンの数は平均1.3個と計算される。このマイクロエマルジョンに市販のヒドラジン1水和物N<sub>2</sub>H<sub>4</sub>・H<sub>2</sub>Oを0.6部加え、室温下に30分間良く攪拌してロジウムイオンをロジウムを含有する超微粒子に還元した。このようにして得られたロジウム含有超微粒子分散液のロジウム含有粒子の粒径は、液滴の大きさ及び液滴中のロジウムイオン数から直径約30Åと推定される。

【0035】前記のロジウム含有超微粒子分散液184部に蒸留水15部を加え、均一になるまで攪拌後に28%アンモニア水で液のpHを8.5~9.5とした。この液に110部のシリコンテトラエトキシドを溶かしてから、これを湯浴で35~40℃に加熱しながらマグネチックスターラーで2時間攪拌を続けた。攪拌していると、加水分解反応でシリカコロイドが形成されて液が濁ってくるから、更にイオン交換水を30部加えて攪拌を2時間継続し、加水分解反応を完結させた。次に、ビーカー内容物を室温まで冷却後に母液を濾別し、得られた沈澱を200部のエタノールで3回洗浄した。該精製沈澱を80℃で12時間乾燥後に空気流通下500℃で4時間焼成し、さらに水素流通下450℃で2時間焼成すると、2.0%のロジウムを含む粒径0.2~0.4μmのシリカゲル19部が得られた。原料シリコンテトラエトキシドからのシリカゲル収率は理論量の62%

で、塩化ロジウムからのロジウム収量は定量的であった。

【0036】以上のようにして調製した2%ロジウム-シリカゲル触媒の性能を評価するために、該触媒を錠剤成形器によって成形して粒径を16~24メッシュとし、この成型触媒を使用する一酸化炭素の水素化反応を行った。すなわち、実施例1と同じ反応器を使って2gの触媒を使用する圧力40kg/cm<sup>2</sup>の気相流通反応を行い、反応温度と反応成績の関係について調べ表2の結果を得た。なお、この評価実験では原料ガスに、一酸化炭素：水素：アルゴン=3：6：1(モル比)の混合ガスを使用し、GHSV6000/h<sub>r</sub>で行った。ここでGHSVとは気体空間速度の略で、1時間に単位容量の触媒上を通過する標準状態の原料ガス容量を意味している。また、この評価実験で使用した白金-シリカ触媒のBET表面積は61m<sup>2</sup>/gであった。

#### 【0037】実施例3

ロジウム含有超微粒子分散液へのシリコンテトラエトキシド添加量を変えた以外は実施例2と同じ方法で4.5%ロジウム-シリカゲル触媒を作製し、実施例2と同じ方法で粒径16~24メッシュの成型触媒としてから、実施例2と同じ評価試験を行った結果を表2に示す。この評価試験は実施例2と同一組成の原料ガスを使い、実施例2と同一圧力で行ったがGHSVは2000/h<sub>r</sub>とした。

#### 【0038】比較例2

比較のために、富士ダヴィソン社製シリカゲルCariact-50に含浸法で2.0%のロジウムを担持させた実施例2と同一粒径の触媒を調製し、GHSVを3000/h<sub>r</sub>とした以外は実施例2と同じ評価試験を行い、表2に示す結果を得た。なお、本比較例の触媒は実施例2の場合と同じ塩化ロジウムを使って作製したものであり、触媒のBET表面積は60m<sup>2</sup>/gであった。

#### 【0039】比較例3

実施例2で製造したロジウム含有超微粒子分散液184部に蒸留水15部を加え、均一になるまで攪拌後に1規定の硝酸で液のpHを3~4とし、この溶液に71部のシリコンテトラエトキシドを溶解してから、実施例2と

同じ方法でシリコンテトラエトキシドの加水分解反応を行った。しかし、この場合は実施例2の場合と異なって沈殿が生成せず、反応器内容物はゼリー状の透明固体となった。この固形物を室温まで冷却後に粉碎して反応器から取り出し、実施例2の場合と同じ方法で良く洗浄後に実施例2の場合と同じ条件で乾燥・空気焼成及び水素還元を行ったところ、2.0%のロジウムを含むシリカゲルが19部得られ、シリコンテトラエトキシドからのシリカゲル収量、及び塩化ロジウムからのロジウム収量\*

\*はほぼ定量的であった。また、得られた触媒はやや透明感のあるガラス状固体で、BET表面積1020m<sup>2</sup>/gであった。この触媒を良く粉碎してから実施例2と同じ方法で成形し、GHSVを1000/hとした以外は実施例2と同じ方法で、一酸化炭素の水素化反応を行った結果を表2に示す。

【0040】

【表2】

	反応温度 (℃)	一酸化炭素 反応率(%)	STY* (g/l・hr)	GHSV (hr <sup>-1</sup> )	BET表面積 (m <sup>2</sup> /g)
実施例2	240	4.3	18	6000	61
	260	9.0	29.1	6000	61
	280	19.4	51.8	6000	61
実施例3	180	5.1	16.3	2000	—
	200	20.5	60.3	2000	—
	220	58.1	248.3	2000	—
比較例2	260	0.9	4.2	3000	60
	280	3.1	16.2	3000	60
	300	9.3	47.2	3000	60
比較例3	240	0.6	trace	1000	1020
	280	1.5	0.2	1000	1020
	300	2.2	0.3	1000	1020

\*触媒量11当たり1時間に生成する炭素数2以上の含酸素化合物の生成量(g)を示す値。

【0041】表2から、実施例の触媒は比較例の触媒より大幅に活性が高いことが明らかであるが、本発明の方法と類似の方法で製造される比較例3の触媒が、含浸法で製造される触媒(比較例2の触媒)より活性が低いことは興味深い。また、実施例の触媒ではロジウム担持量の多い実施例3の触媒が優れており、該触媒を使った実験で得られるSTY248.3g/l・hrは、一酸化炭素の水素化による炭素数2以上の含酸素有機化合物製造方法として、現在までに得られているデータの中で最高値である。なお、表2から一酸化炭素を水素化するロジウム触媒における活性差は、表面積の差によるものではないことが明らかである。

【0042】実施例4

内容積11のビーカーに、メタバナジン酸アンモニウム3.5部と蒸留水50部とシュウ酸7.46部を採り、攪拌しながら80℃に加熱して均一液とした。この液を室温に冷却後、これにリン酸二水素アンモニウム3.4部を均一溶解させ、この液に1規定の希硝酸を加えて液のpHを3~4に調整した。このpH調整は、前記の混

30 合液を原料としてマイクロエマルジョンを調製する際に、リン酸二水素アンモニウムが沈殿するのを防ぐためのpH調整である。前記の混合液に、シクロヘキサン390部と実施例1で使用したものと同一界面活性剤110部を加え、室温(25℃)下にマグネティックスターラーで攪拌したところ、100g中にリン0.16gとバナジウム0.26gを含有するマイクロエマルジョンがすぐ生成した。該マイクロエマルジョンは一相系油中水滴型であり、液滴の平均直径は45Åと計算されるから、個々の液滴中に含まれるリン及びバナジウムの原子数は両者とも平均11個と計算される。このマイクロエマルジョンに28%アンモニア水を加えてpHを9~9.5とし、室温で30分間攪拌してリン及びバナジウムを含有する超微粒子分散液を作製した。

40 【0043】前記分散液190部に蒸留水5部を加えて良く攪拌し、pHが9~9.5に保たれている前記の水で希釈された分散液にシリコンテトラエトキシド60部を溶解させ、この液を40~45℃で2時間攪拌した。その結果、シリコンテトラエトキシドが加水分解されてシリカコロイド沈殿が生成してくるから、加水分解反応を完結させるためにアンモニア水でpHを9に調整した

蒸留水を30部加え、さらに2時間撹拌を続けた。反応終了後、生成物を室温まで冷却してから母液を濾別し、得られた沈殿を200部のエタノールで3回洗浄して沈殿に含まれている界面活性剤や有機溶媒を十分に除去した。この沈殿を80℃で12時間乾燥してから空気流通下に500℃で4時間焼成すると、11%のVOPO<sub>4</sub>を含むシリカゲル11部が得られた。原料シリコンテトラエトキシドからのシリカゲル収率は理論量のほぼ60%で、メタバナジン酸アンモニウム及びリン酸二水素アンモニウムからのVとPの収率は理論量のほぼ90%であった。なお、生成したVOPO<sub>4</sub>担持シリカゲルのBET表面積は38m<sup>2</sup>/gであった。

【0044】上記の方法で調製した11%VOPO<sub>4</sub>、シリカゲル触媒の性能を評価するため、該触媒を錠剤成形器で成形して粒径を16~24メッシュとし、この成形触媒3gを内径17mmの反応管（実施例1で使用了のものと同じ物）に装填してイソブタンの空気酸化特性を調べた。すなわち、実施例1で使用了のものと同じ電気炉内に反応管を設置し、この反応管に、イソブタン：酸素：ヘリウム=1：1：3（容量比）の混合ガスを60ml/分の速度で送入し、触媒層温度（反応温度）と反応率の関係、及び触媒層温度と〔メタクロレイン（M\*

\*AL）+メタクリル酸（MAA）〕選択率の関係等を求め、表3の結果を得た。なお、反応生成物の分析はガスクロマトグラフ法で行った。

#### 【0045】比較例3

比較のため、常法で製造した含浸法の11%VOPO<sub>4</sub>、シリカゲル触媒3gを使用し、実施例4と同一条件でイソブタン酸化を行い、表3に併記した結果を得た。この比較例で使用了した触媒は、比較例1で使用了したものと同じシリカゲルを担体とし、これにバナジン酸アンモニウムとリン酸二水素アンモニウムを常法によって担持させてから、空気の流通下に焼成して調製したものであり、BET表面積61.0m<sup>2</sup>/gの触媒である。

#### 【0046】比較例4

比較例3とは別の比較例として、文献〔J.SHIMODA, Bu11. Chem. Soc. Jpn. 582163~2171(1985)〕に記載されている方法に従って、五酸化バナジウムと塩酸ヒドロキシルアミンとリン酸を出発原料にして調製したピロリン酸バナジル3gを触媒とし、実施例4の場合と同じ方法でイソブタンを酸化させた実験結果を表3に示す。

#### 【0047】

【表3】

	反応温度 (℃)	反応率 (%)	反応生成物の選択率 (mol %)		
			MAL + MAA	酸化生成物*	CO + CO <sub>2</sub>
実施例4	350	0.6	75.7	9.1	15.2
	400	2.0	61.2	8.3	28.0
	450	5.1	44.8	8.6	43.4
比較例3	300	3.2	3.5	10.4	84.0
	350	21.1	1.0	6.5	91.4
	400	21.7	1.4	7.8	89.2
比較例4	300	0.5	45.9	12.9	41.2
	350	3.2	18.1	16.7	62.9
	400	11.5	8.1	11.8	78.0

\*MAL+MAA及びCO+CO<sub>2</sub>を除いた酸化反応生成物で、無水マレイン酸やC<sub>3</sub>の酸化生成物が含まれている。

【0048】表3から、本発明の触媒は比較例のそれより大幅に（MAL+MAA）選択率が高いことが分る。例えば、従来のイソブタン酸化用触媒のうちでは部分酸化活性が高い触媒として注目されている比較例4に記載した触媒の使用時は、反応率0.5%で（MAL+MAA）選択率が45.9モル%、反応率3.2%では（MAL+MAA）選択率が18.1モル%なのに、本発明の触媒を使用する実施例4の結果では、反応率0.6%

で（MAL+MAA）選択率が75.7モル%、反応率2.0%では（MAL+MAA）選択率が61.2モル%を示している。また、本発明の触媒は完全酸化抑制型触媒と云え、通常の含浸法で調製された比較例3の触媒使用時には、反応率3.2%で（CO+CO<sub>2</sub>）選択率が84.0%モルとなるのに、本発明の触媒を使用する実施例4の実験結果では、反応率5.1%でも（CO+CO<sub>2</sub>）選択率が43.4モル%にすぎないことが分る。

#### 【0049】

【発明の効果】本発明の方法で製造される担持触媒は、



超微粒子を均一分散した分散液中で金属アルコキシドを加水分解する方法で製造され、加熱等で該超微粒子が凝集しにくいことから、高機能で使用中の劣化が少ない担\*

\* 持触媒である。従って、該触媒は従来法で製造される担持触媒より高機能で長寿命である。

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